Introduction to Analytical Analysis Instrumentation

Jully Tan
School of Engineering

Learning Outcome

- At the end of this chapter, students are able to:

- Review of the Analytical Strategy
- Instrumental Analysis Methods
- Basic of Instrumental Measurement
- Preparation of Standards
- Blanks and Controls
- Laboratory Data Acquisition & Information Management

Introduction of Analytical Chemistry

- Analytical chemistry ***is the branch of chemistry that deals with the separation, identification and determination of components in a sample.***
- The method of the analysis is **qualitative** (identification) or **quantitative**.
  - Qualitative analysis is **identification**.
  - Quantitative analysis, is the analysis of a material for **how much** of one or more components is present.
- **Analysis procedures** can be **additionally classified** into procedures that involve:

  - **Physical properties**
  - **Wet chemical analysis** procedures
  - **Instrumental chemical analysis** procedures

Errors, Statistics & Statistical Control

Analytical Errors

- Errors in the analytical laboratory are basically of 2 types:
  - ☐ Determinate errors
  - ☐ Indeterminate errors
- **Determinate errors**:
  - ☐ Also called **systematic errors**
  - ☐ Are **errors** that **were known** to have occurred
  - ☐ May arise from **unavoidable sources** (contamination, reagent impurities, poor sampling techniques, errors in calculation, etc)
- **Indeterminate errors**:
  - ☐ Also called **random errors**
  - ☐ Are **errors** that are **not specifically identified** and impossible to avoid
  - ☐ So a **statistical analysis** must be performed to determine whether the results are far enough **“off-track”** to merit rejection.

Determinate errors (systematic error):

(1) *Equipment errors*

- are ascribed to **deficiencies in the quality of the apparatus** used in carrying out the experiment: instruments, glassware, reagents and so forth.
- e.g. the balance is not functioning properly, a reagent contains a reactive impurity, a solvent is impure.

(2) *Personal errors*

- result from the **carelessness, inattention, or personal limitations** of the experimenter.
- e.g. transfer of solutions, incomplete drying of samples, not waiting for a sample to reach the balance temperature before weighing it, and incomplete mixing of solution.

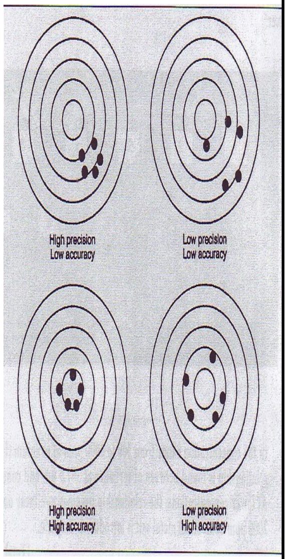
(3) *Method errors*

- Are **chemical or physicochemical in nature** and lie in a property of the system being studied.
- e.g. include the incomplete reactions, solvent evaporation, impurities in reagent and others.
- The most serious errors of an analysis
- Most of the above errors can be minimized or corrected for, but errors that are inherent in the method cannot be changed unless the conditions of the determination are altered.

Elementary Statistics

- The indeterminate errors manifest themselves in values that deviate, positively and negatively, from the mean of all the values obtained.
- **Mean (m)**
- **Deviation (d = m – e)**
- **Standard deviation (s)**
- **Relative standard deviation, RSD (s/m)**

Precision and Accuracy



- **Precision** refers to:
  - ☐ The repeatability of a measurement.
  - ☐ Measurement deviate slightly from one another – high degree of precision
  - ☐ But such data may or may not represent the real value of that parameter.
  - ☐ In other words, it may not be accurate.
- **Accuracy** refers to:
  - ☐ Correctness of a measurement or how close it comes to the correct value of a parameter.
- For example, if an analyst has an object that weighs exactly 1.0000 g, the accuracy of a laboratory balance can be determined. If
  - ☐ If 0.9998 and 1.0002 g – both precise and accurate
  - ☐ If 0.9983 and 0.9987 g – the balance is precise but not accurate
  - ☐ If 0.9956 and 0.9991 g – the data are neither precise nor accurate
  - ☐ If 0.9956 and 1.0042 g – the balance is not precise but accurate

Parameters Characterizing Instrumental Techniques

Detection Limit

- The **smallest amount of an analyte** giving a **detector response** significantly different from a **blank** or **background response**.
- i.e. the response from standards containing the same reagents and having the same overall composition (matrix) as the samples, where this is known, but containing no analyte.
- The concentration that gives a **signal equal to 3 times** the **standard deviation** of the background.
- Are usually based on estimates of the standard deviation of replicate measurements of prepared blanks.

Selectivity

- The ability of a methodology or instrumentation to respond to a **specific analyte** and **not to other species** in a given sample matrix.
- Ability to discriminate between the species of interest and possible interferences.
- If the response is distinguished from all other responses, the method is said to be selective.

Specificity

- Refers to a method that produces a response for a **single analyte only**.
- There are very **few methods** that respond to **only one analyte**.
- Is generally considered to be 100% selectivity.
- It is necessary to establish the fact that the signal produced at the measurement stage, which was attributed to the analyte, is only due to the analyte and not from the presence of something chemically or physically similar or arising as a coincidence.
- Expressed in terms of the ability to detect and quantify specific food constituents even in the presence of similar compounds, e.g, the estimation of individual sugars present in a food containing a range of both reducing and non-reducing sugars.

Sensitivity

- The ability of a methodology or instrumentation to discriminate among samples containing different amounts of analyte; the change in analyte signal with a corresponding change in analyte concentration.

- Modern methods of food analysis such as **gas chromatography** enable detections to be obtained at levels as low as **10^{-10}g.**

- While more established **colorimetric methods** are sensitive to levels of around **10^{-7}g.**

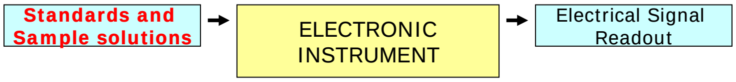
- **Traditional methods** of **gravimetric and titrimetric analysis**, on the other hand, may only allow measurements to levels of around **10^{-3}g.**

Analytical Strategy

- The process by which an **analyte's identity** or the **concentration level** in a sample is determined in the laboratory may involve **many individual steps**.
- **Analytical Strategy** consist of five parts:
  1. Sampling
  2. Sample Preparation
  3. The analytical method
  4. Data handling
  5. The calculation and reporting of results

Instrumental Analysis Methods

- **Quantitative instrumental analysis** mostly involves sophisticated electronic instrumentation that generate electrical signals that are related to some property of the analyte and proportional to the analyte’s concentration in a solution.



- In other words,
  1. The standards and samples are provided to the instrument
  2. The instrument measures the property
  3. The electrical signal is generated
  4. The signal (numerical value of the property itself) displayed on a readout
  5. The calculation of the analyte’s concentration based on **standard curve**

- The standards and sample solutions are introduced to the instrument in a variety of ways. For examples, in the case of:

  - pH meter, one or two probes are immersed in the solution.

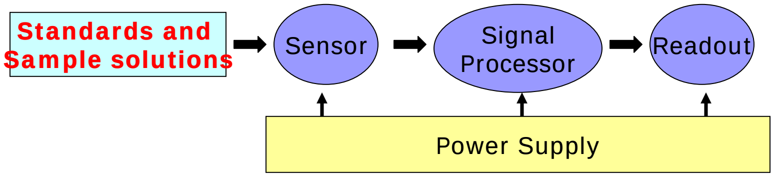
  - Refractometer, a small quantity of the solution is placed on a prism at the bottom of a sample well inside the instrument

  - Spectrophotometer, the solution is held in a round (like a test tube) or square container called a cuvette.

Basic of Instrumental Measurement

- In general, an instrument consists of four components:

  1. **Sensor** – converts a property of the solution into a weak electrical signal.
  2. A signal processor - amplifies or scales the signal and convert it to a usable form
  3. **Readout device** – displays the signal for the analyst to see
  4. Power supply – provide the power to run these three components



- The information flow within the instrument occurs with the movement of **electrons, or electrical current**.

Preparation of Standards

- The series of standard solutions of the analyte can be prepared through several **dilutions of a stock (primary) standard solution**.
- The **stock (primary) standard** may be prepared by:
  1. The analyst or purchased from a chemical vendor
  2. Weighing a quantity of the primary standard analyte chemical into a volumetric flask and diluting to the mark.
- It may also be a **secondary standard** prepared by diluting a primary stock that was purchased from a chemical vendor or prepared in the lab.
- Another is a so-called **serial dilution** procedure, eg. The second solution is prepared by diluting the first, etc.
- Both **volumetric flasks** and suitable **solution transfer devices** are required.

Blanks and Controls

- The **blank** is a solution that contains all the substances present in the standards, and the unknown if possible, except for the analyte.
- The readout for such a solution should be zero, and is often adjusted to read zero when this blank is being measured.
- Thus, the blank is useful as a sort of pre-calibration step the instrument and is appropriately called a **reagent blank**.
- While a reagent blank is frequently prepared and used as described above, a sample blank is sometimes appropriate instead.
- A **sample blank** takes into account any **chemical changes** that may take place as the sample is taken or prepared.
- A **control** is a standard solution of the analyte prepared independently, often by other laboratory personnel, for the purpose of cross-checking the analyst's work.
- The analyst then knows to scrutinize his or her work for the purpose of discovering an error.
- Thus, the **problem can be traced** to a bad analyst (**human error**), instrument (**instrument error**), or other component of the procedure such as bad reagent (**method error**).
- A control can be divided into **positive** and **negative** control.